# Mechanism of Thermal Decomposition of Tetra-aryltellurium Species

By **Stephen A. Glover**, Organic Chemistry Research Laboratories, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth, South Africa and Department of Chemistry, Imperial College, London SW7 2AY

Tetra-aryltellurium species decompose upon heating giving good yields of diaryl tellurides and biphenyls. Radical-scavenging experiments show that phenyl radicals are not intermediates in the formation of biphenyls. In contrast, cross-over experiments give mixed biphenyls as well as mixed diaryl tellurides, but these are formed by a statistical redistribution of organic groups giving mixed tetra-aryltellurium species which decompose thermally in an indiscrimate fashion.

RESEARCH in the field of organo-tellurium chemistry has been limited relative to that of other group 6 elements, and of the reactions and species documented,[1,2] the majority pertain to diorganyl tellurides, diorganyltellurium dihalides, and triorganyltelluronium salts. A minor portion of studies thus far have dealt with the class of tetra-organotellurium compounds in which tellurium is bonded directly to carbon.

Recently we reported on the nature of the decomposition reactions of tetra-aryl telluriums.[3] The study was prompted by the observation that tetraphenyltellurium (1) and tetrakis(pentafluorophenyl)tellurium (2) [4,5] decompose upon heating (>100 °C) giving the corresponding diaryl tellurides and biphenyls along with some benzene [in the case of (1)], Hellwinkel and Fahrbach also showed that bis-(2,2'-biphenylylene)telluriums (3)


(1) R = Ph

(2) R = C$_6$F$_5$
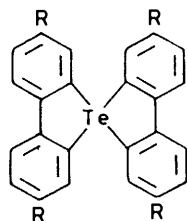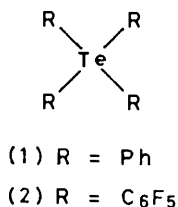
(3) R = H

(4) R = Me
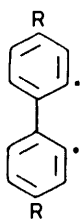
(5)

and (4) decomposed at higher temperatures (>200 °C) to dibenzotellurophenes and products derived from the diradical (5) such as biphenylenes, tetraphenylenes, and, in the case of (4), 4,4'-dimethylbiphenyl.[6] 2,2'-Biphenylylene dimethyl and dibutyl tellurium likewise afforded dibenzotellurophene together with monomeric and dimeric alkanes.[7] Whilst the bis(phenylylene)tellurium species (3) and (4) must decompose via a free radical pathway (pathway A, Scheme 1), the same cannot be

said for the tetraphenyltelluriums (1) and (2), since biphenyls could be formed in a geminate reaction or by a concerted decomposition (Scheme 1, pathway B). To distinguish between these two modes of reaction, tetra-
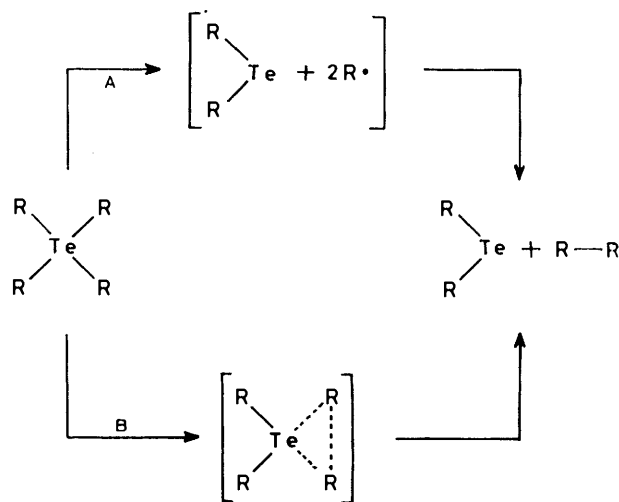
SCHEME 1

phenyltellurium, synthesised in good yields from tellurium tetrachloride and lithium bromide-free phenyl-lithium,[4] was decomposed under a variety of conditions (Table 1). The yields of geminate combination of
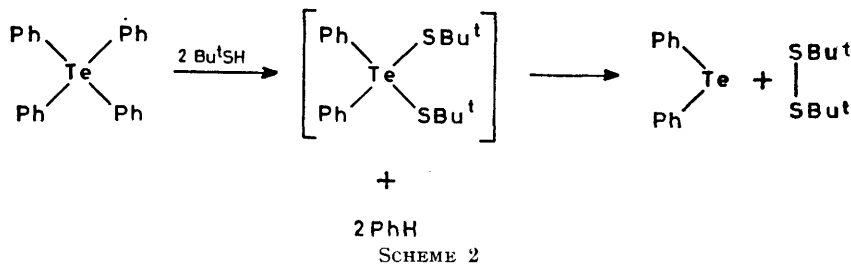
TABLE 1

Decomposition reactions of tetraphenyltellurium

| | | Conversion (%) [a] | | |
| | | Benzene (± 2) | Diphenyl telluride (± 5) | Biphenyl (± 3) |
Reaction	Conditions			
(i)	No solvent (*in vacuo*)	10	92	89
(ii)	Toluene (N$_2$)	11	96	101
(iii)	Triethylsilane (N$_2$)	b	80	90
(iv)	Furan (N$_2$)	16	94	85
(v)	Styrene (N$_2$)	b	103	95
(vi)	t-Butyl hydrosulphide	114 [c]	105	0

[a] Determined by g.l.c. [b] Not estimated. [c] Larger error limits. Reaction carried out at room temperature (2 h).

radicals, inferred in pathway A, were expected to decrease sharply for decompositions carried out in reactive solvents.[8] Noticeably, however, the yields of biphenyl and diphenyl telluride from decomposition at 140 °C in the hydrogen-atom sources toluene and triethylsilane

and the known phenyl-radical scavengers furan[9] and styrene, did not differ significantly from the neat reaction. Surprisingly, no biphenyl was formed from thermolysis in t-butyl hydrosulphide and it was found (t.l.c.) that even at room temperature, tetraphenyltellurium reacted rapidly with t-butyl hydrosulphide giving quantitative yields of diphenyl telluride, di-t-butyl disulphide, and benzene. A heterolytic replacement reaction followed by radical or concerted decomposition is envisaged (Scheme 2) although alternative mechanisms cannot be ruled out. Only traces of polymer were formed from

the melt and in a two-to-one mixture of benzene-1,4-dihydrobenzene, an excellent hydrogen atom source,[11] are shown in Table 2. The indifference of the course of reaction to hydrogen-donor solvent was emphasised by the formation of toluene (80%) along with triphenyl-methane (100%) upon homolysis of tolylazotriphenyl-methane in benzene-1,4-dihydrobenzene.

The results of decomposition of tetraphenyltellurium and tetrakis-(4-methylphenyl)tellurium under different conditions thus disfavour radical decomposition as the major pathway (pathway A, Scheme 1). A radical de-

Scheme 2

the thermolysis in styrene monomer. In contrast a control experiment with an equimolar amount of dibenzoyl peroxide gave 77% of non-volatile material.

The decomposition products from thermolysis of

(7)   (6)
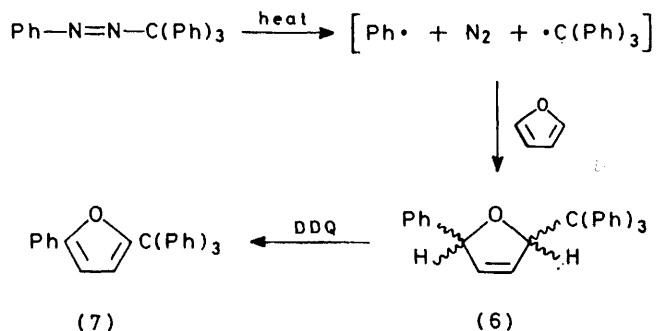
tetraphenyltellurium in toluene and furan differed markedly from those formed from phenylazotriphenyl-methane (PAT) which is a good source of phenyl radicals.[10] Both substrates decomposed smoothly at 80° but in toluene, two equivalents of PAT produced tri-phenylmethane (38%), benzene (56%), diphenylmethane (19%), o-phenyltoluene (8.5%), and p-phenyltoluene (4.5%) while in furan, isomeric 2-phenyl-5-triphenyl-methyl-2,5-dihydrofurans (6) (62%) were isolated and were readily oxidised by 2,5-dichloro-3,6-dicyanobenzo-quinone (DDQ) to the known disubstituted furan (7).[9] This difference in reactivity indicated conclusively that phenyl radicals were not common to both decompositions.

Tetrakis-(4-methylphenyl)tellurium, prepared in 52% yield from tellurium tetrachloride and lithium bromide-free 4-methylphenyl-lithium was a yellow crystalline material which, like its parent compound, decomposed upon melting (124—127 °C) to give similar quantities of 4,4'-dimethylbiphenyl and bis-(4-methylphenyl)telluride as well as some toluene. The results of decomposition in

composition would have to imply that even in radical-intercepting solvents a geminate reaction occurs to the exclusion of almost all other free-radical processes. By comparison the cage recombination of cyanopropyl radicals from homolysis of azobisisobutyronitrile was limited to less than 35% in pure styrene.[8] Furthermore, were pathway A operative, lower yields of biphenyl would be expected since radical-cage recombination would be disfavoured by the large initial separation of the phenyl radicals, which is known to impede geminate reactions.[8]

By analogy with the diaryltellurium dihalides, the tetra-aryltelluriums would be expected to adopt a tri-gonal bipyramidal structure with an equatorial lone pair (8).[1,*] Bidentate ligands of the bis(biphenylylene) tellurium species must each occupy an equatorial and an axial position (9).[1] Pearson has shown that concerted

TABLE 2

Decomposition reactions of tetrakis-(4-methylphenyl)-tellurium

Reaction[a]	Toluene (% conversion)	Ratio 4,4'-dimethylbiphenyl : bis-(4-methylphenyl) telluride
Tol₄Te (N₂)	15	0.83 : 1
Tol₄Te + 1,4-dihydro-benzene (N₂)	12.5	0.94 : 1

[a] Tol = 4-MeC₆H₄.

apical or equatorial coupling of ligands is a symmetry allowed process for trigonal bipyramidal structures whilst axial–apical coupling is essentially forbidden.[12] Mole-

$$R_2SX_2 \rightleftharpoons R_2S + X_2 \qquad (1)$$
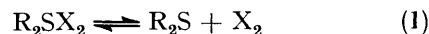
cules of the type R_2SX_2 and their selenium and tellurium counterparts probably exist in the rapid equilibrium (1)
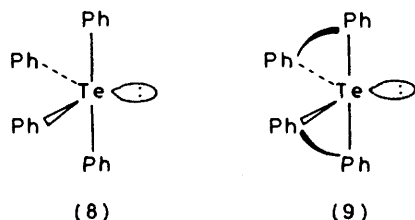
* Tetrakis-(4-methylphenyl)tellurium was too unstable for a structural determination using X-ray methods.

as a result of concerted addition and dissociation.[12] It is considered therefore that the decomposition of tetraphenyltellurium species is a symmetry-allowed concerted process (Figure) and has an analogy in the reaction of triarylsulphonium salts with optically active alkyl-lithium reagents (2). This reaction proceeds *via*

$$Ar_3S^+ + R^*Li \longrightarrow Ar_2S + Ar-R^* \qquad (2)$$

the sulphuran Ar_3SR intermediate which decomposes with retention of configuration at R.[12] Interestingly, the decomposition of bis(phenylylene)telluriums (4) and (5), in which concerted coupling would be forbidden, react at high temperature (>200 °C) *via* a free-radical process.

The results of radical-scavenging experiments contrasted with those from cross-over experiments.

Ph
|
Ph···Te ⊂:⊃
Ph◁ |
Ph

(8)

Ph
|
Ph:···Te ⊂•:⊃
Ph |
Ph

(9)

Thermal decomposition of mixtures of tetraphenyltellurium and tetrakis-(4-methylphenyl)tellurium *in vacuo* or in toluene under nitrogen gave, along with the expected symmetrical diaryl tellurides and biphenyls, extensive amounts of 4-methylbiphenyl and phenyl 4-methylphenyl telluride. The relative amounts of symmetrical and unsymmetrical products were determined from peak areas in the gas–liquid chromatogram of the crude mixture. Pentadeuteriobiphenyl and phenyl-pentadeuterio-phenyltellurium were also formed together with symmetrical products from simultaneous thermolysis *in vacuo* of tetraphenyltellurium and tetrakis-(pentadeuteriophenyl)tellurium. The biphenyl and telluride fractions were isolated by preparative g.l.c. and analysed by mass spectroscopy.

At first sight, the formation of a mixture of tellurides from the simultaneous decomposition of tetraphenyl- and tetrakis-(4-methylphenyl)-tellurium in toluene might have implied diffusion of aryl radicals from the solvent cage with subsequent reaction upon a tetra-aryl or diaryl tellurium species, the former yielding mixed telluride upon decomposition. Radical-displacement reactions at the oxygen and sulphur atoms in peroxides and disulphides, respectively, are known.[13] However, since aryl radicals could not be trapped in the decomposition of either substrate, it is proposed that mixed products arise by a rapid random interchange of aryl ligands prior to decomposition. Analogous non-radical ligand-exchange reactions have been reported for organolead and organomercury compounds.[14-17]

A random redistribution of organic groups R^1 and R^2 between two tetravalent tellurium species $R^1{}_4Te$ and $R^2{}_4Te$ whose mole fractions are r_1 and r_2 respectively, should lead to five distinct species whose mole fractions

are shown in Scheme 3.[14] Based upon the assumption that each species can decompose by four equivalent processes (*i.e.* formation of mixed or symmetrical biphenyls and diaryl tellurides have similar activation energies) the resultant mole fractions of each thermolysis product can be deduced (Scheme 3). These were in reasonable
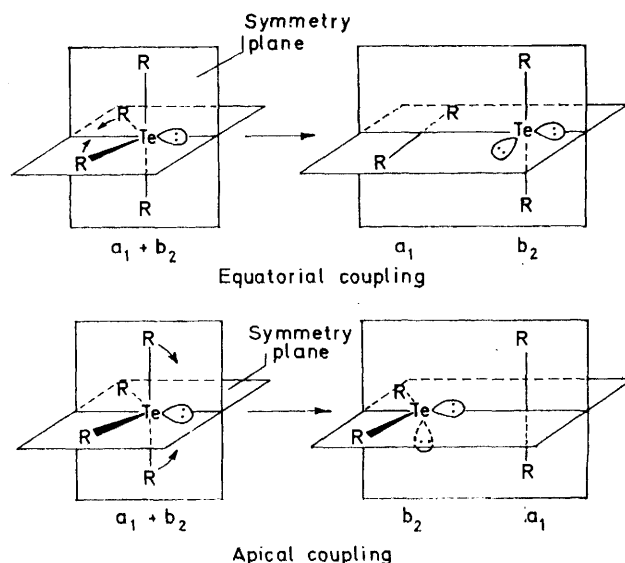

FIGURE Symmetry correlations for concerted decomposition of tetra organyl tellurium; a_1 and b_2 refer to the symmetry of the σ-bonds broken and σ-bond and lone pair formed with respect to the symmetry element; a_1 = symmetrical, b_2 = anti-symmetrical.

agreement with the experimentally determined values from the three cross-over experiments (Table 3).

The assumption of equivalent decomposition pathways for tetra-aryl telluriums appears to be valid in the case of the tetraphenyltellurium–tetrakis(pentadeuteriophenyl)-tellurium experiments. However, in the decomposition

TABLE 3

Relative yields of products obtained from cross-over experiments using tetraphenyltellurium with tetrakis-(4-methylphenyl)- and tetrakis(pentadeuteriophenyl)-tellurium
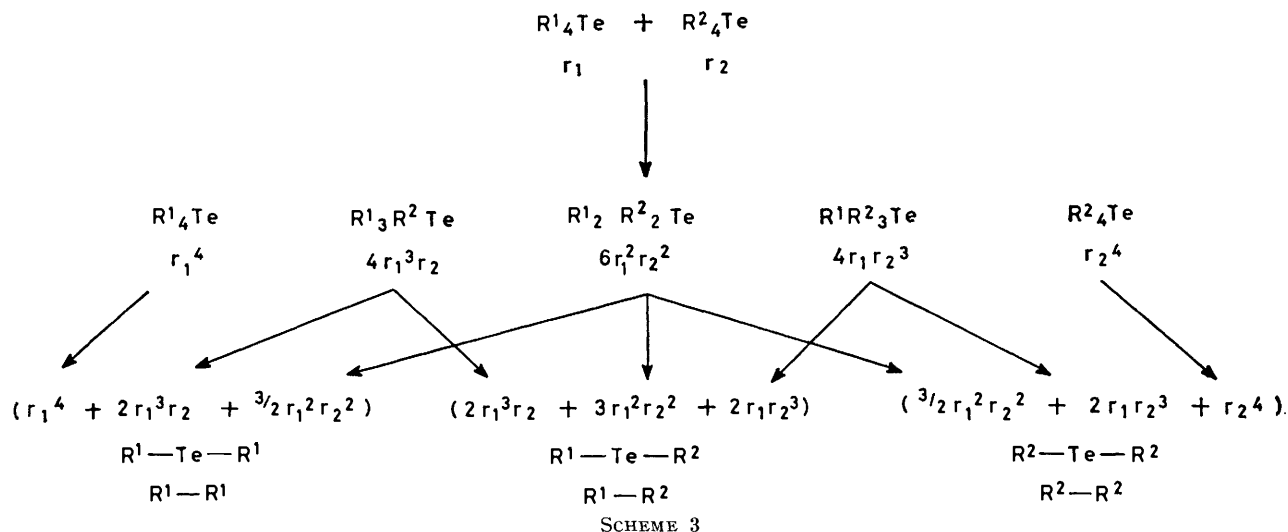
Reaction [a]		$R^1 = R^2$ = Ph	$R^1 = Ph$, R^2 = Tol	$R^1 = R^2$ = Tol
Ph_4Te	R^1TeR^2	0.27	0.45	0.26
Tol_4Te	Calc.	0.38	0.42	0.19
in vacuo	R^1-R^2	0.43	0.43	0.12
Ph_4Te +	R^1TeR^2	0.21	0.52	0.26
Tol_4Te	Calc.	0.32	0.43	0.24
in toluene (N_2)	R_1-R_2	0.31	0.49	0.19
		$R^1 = R^2$ = Ph	$R^1 = Ph$, $R^2 = C_6D_5$	$R^1 = R^2$ = C_6D_5
Ph_4Te +	R^1TeR^2	0.33	0.47	0.19
$(C_6D_5)_4Te$	Calc.	0.398	0.42	0.18
in vacuo	R^1-R^2	0.41	0.42	0.15

[a] Tol = $4-MeC_6H_4$.

of the random mixture from tetraphenyltellurium and tetrakis-(4-methylphenyl)tellurium, formation of bis-(4-methylphenyl) telluride would appear to be more favourable than decomposition into diphenyl telluride. There is correspondingly less bitolyl and more biphenyl

than predicted. The exchange of organic groups did not occur upon heating diphenyl telluride and bis-(4-methylphenyl) telluride. However some mixed telluride and biphenyl were obtained when tetrakis-(4-methylphenyl)tellurium was decomposed in diphenyl telluride.

tellurium species and other organometallic agents such as alkyl-lithiums or Grignard reagents cannot be excluded. Some evidence in this regard was found from the reaction of diphenyltellurium dichloride with an excess of β-phenylethylmagnesium bromide. Treatment of the reaction

$$R^1{}_4Te \; + \; R^2{}_4Te$$
$$r_1 \qquad\qquad r_2$$

$R^1{}_4Te$	$R^1{}_3R^2Te$	$R^1{}_2 R^2{}_2 Te$	$R^1R^2{}_3Te$	$R^2{}_4Te$
$r_1{}^4$	$4r_1{}^3r_2$	$6r_1{}^2r_2{}^2$	$4r_1r_2{}^3$	$r_2{}^4$

$$(r_1{}^4 + 2r_1{}^3r_2 + {}^3\!/_2 r_1{}^2r_2{}^2) \qquad (2r_1{}^3r_2 + 3r_1{}^2r_2{}^2 + 2r_1r_2{}^3) \qquad ({}^3\!/_2 r_1{}^2r_2{}^2 + 2r_1r_2{}^3 + r_2{}^4).$$

$$R^1—Te—R^1 \qquad\qquad R^1—Te—R^2 \qquad\qquad R^2—Te—R^2$$
$$R^1—R^1 \qquad\qquad\qquad R^1—R^2 \qquad\qquad\qquad R^2—R^2$$

SCHEME 3

The rapid exchange of ligands between tetra-aryltellurium species is proposed to occur by a series of equilibria involving the lone pair and equatorial or axial ligands (Scheme 4). The interchange of axial with equatorial

mixture with dilute hydrochloric acid after 15 min gave mainly tris-(β-phenylethyl)telluronium bromide and some tris-(β-phenylethyl)telluronium chloride along with low yields of 1,4-diphenylbutane (13%) and diphenyl
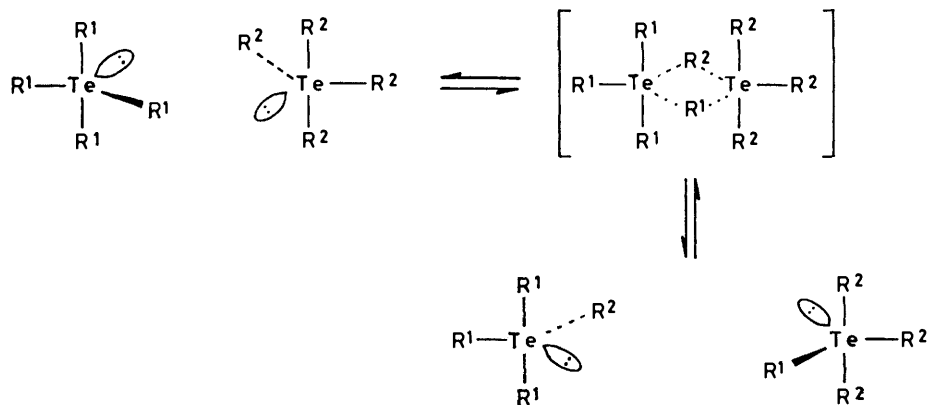
SCHEME 4

groups through mutarotation has been suggested by Hellwinkel and Fahrbach to explain the equivalent chemical shifts, even at low temperature, of the four methyl groups of bis-(4,4'-dimethylbiphenylylene)tellurium (4).[6] The same arguments could be applied to tetrakis-(4-methylphenyl)tellurium which displays a single methyl resonance (δ 2.0) in its n.m.r. spectrum. Here, however, the equivalence can also be attributed to the dynamic redistribution of tolyl groups in solution. Similar arguments suggest that mixed tetra-organyltellurium species (10) and (11) in solution would most probably result in mixtures, the composition of which would be determined by the exchange reaction. Furthermore the possibility of ligand exchange between organo-

telluride. Prolonged stirring at room temperature followed by gentle heating raised the yield of 1,4-diphenylbutane to 30%, but the main products were still

(10)   (11)

the tris-(β-phenylethyl)telluronium salts. The isolation of telluronium salts indicated a rapid displacement of the phenyl groups from diphenyltellurium dichloride to give either tris-(β-phenylethyl)telluronium halide or tetrakis-

(β-phenylethyl)tellurium which decomposed slowly at room temperature. However, the exact nature of these reactions warrants further study.

EXPERIMENTAL

Melting points were determined on a Kofler hot stage. I.r. spectra were measured with a Perkin-Elmer 157 spectrometer. N.m.r. spectra were recorded on either a Varian T60 or Varian EM360A n.m.r. spectrometer with tetramethylsilane as internal standard. Mass spectra were obtained with an A.E.I. MS9 high-resolution mass spectrometer. Silica gel for preparative plates was Merck GF$_{254}$. Analytical gas–liquid chromatograms were obtained using a Perkin-Elmer F11 gas chromatograph fitted with a flame-ionisation detector. The following columns were used: column A (benzene and toluene determinations), squalane on Chromosorb P, 80—100 mesh; column B (biphenyl, diphenyl telluride, and di-t-butyl disulphide determinations), fluorosilicon oil on Chromosorb W, 80—100 mesh. Preparative gas–liquid chromatography was carried out on an Aeograph Autoprep A700 chromatograph with manual collection using column C (SE30 on Chromosorb W, 60—80 mesh).

Diphenylmercury, bis(pentadeuteriophenyl)mercury, and bis-(4-methylphenyl)mercury were prepared by literature procedures.[18] Ethereal aryl-lithium solutions (free from lithium halide) were prepared from the corresponding diarylmercury compounds and lithium,[19] and were standardised by titration with butan-2-ol in xylene or benzene under nitrogen using 1,10-phenanthroline as indicator.

Tetraphenyl tellurium.—A solution of phenyl-lithium (10.5 ml; 1N) was added dropwise to a cold (−70 °C), well stirred suspension of tellurium tetrachloride (0.51 g) in anhydrous ether (3 ml) under an inert atmosphere. The mixture was warmed to room temperature (30 min) and centrifuged. The yellow ethereal solution was decanted under nitrogen and concentrated in a stream of nitrogen. The yellow crystals which formed on cooling (−70 °C) were filtered in a closed system, washed once with cold ether (3 ml), and handled in an inert atmosphere (0.571 g, 70%), m.p. 98—102° (decomp., softening from 60°) (lit.,[4] m.p. 100—102°), m/e 361, 284, 207, 154, and 77. An optimum crude yield of 83% was obtained on a 1-g scale.

By the same general method were prepared tetrakis-(pentadeuteriophenyl)tellurium, yellow prisms, m.p. 102° (decomp.), yield 25%, characterised by study of its decomposition products, and *tetrakis-(4-methylphenyl)tellurium* (52% yield), yellow prisms, m.p. 139—144° (decomp., softening from 135°), δ (C$_6$D$_6$) 2.0 (12 H, s), 6.78 (8 H, d, J 8 Hz), and 7.32 (8 H, d, J 8 Hz), m/e 403, 312, 182, 167, and 91 [Found (crude material): C, 67.7; H, 5.45. C$_{28}$H$_{28}$Te requires C, 68.35; H, 5.7%].

Diphenyl tellurium dichloride[1] and diphenyl telluride[1] were synthesised by literature procedures.

Decomposition of Tetraphenyltellurium.—Tetraphenyltellurium (ca. 100 mg) (dried in vacuo in the dark at room temperature) was sealed in ampoules either in vacuo or in a solvent (1 ml) under dry nitrogen. Unless otherwise specified, the ampoule was heated to 140 °C in an oil-bath, cooled to −70 °C, and opened. The contents were made up with the respective solvents to 2 ml in a volumetric flask and analysed for benzene, biphenyl, and diphenyl telluride by comparison of peak heights with those of standard solutions of benzene in toluene, biphenyl in toluene, and diphenyl telluride in benzene. The results appear in Table 1.

Reaction mixtures from (i), (ii), (iii), (iv), and (v) displayed a single base line component on silica gel [light petroleum (b.p. 40—60°)] prior to reaction and, after heating, both diphenyl telluride and biphenyl. Reaction mixture (vi) displayed both diphenyl telluride and di-t-butyl disulphide immediately after addition of t-butyl hydrosulphide. The constituents (t.l.c.) were unaltered on heating to 140 °C or on standing at room temperature for 2 h. Di-t-butyl disulphide was determined by comparison of peak heights on g.l.c. with those of standard solutions of di-t-butyl disulphide in ether.

Decomposition of Tetrakis-(4-methylphenyl)tellurium.—Tetrakis-(4-methylphenyl)tellurium (0.266 4 g) was sealed in vacuo and heated in an oil-bath to its m.p. [124—127° (decomp., softening from 120°)]. The ampoule was cooled (−70 °C) and opened, and the resulting oil, δ (C$_6$D$_6$) 2.04 (6 H, s), 2.2 (6 H, s), 6.77, and 7.6 (8 H, 2 × d, J 8 Hz), and 7.06 and 7.43 (8 H, 2 × d, J 8 Hz), was a mixture (n.m.r., t.l.c., g.l.c.) of two equal components which were separated by preparative g.l.c. The component with shorter retention time (column C) was a solid (0.053 g) which crystallised from ether as needles of bitolyl, m.p. 120—121° (lit.,[20] 121°), δ (CDCl$_3$) 2.38 (6 H, s) and 7.18 and 7.48 (8 H, 2 × d, J 9 Hz), M$^+$ 182, m/e 167 and 91. The second component was a solid (0.062 g) which crystallised from ether as colourless needles of bis-(4-methylphenyl) telluride, m.p. 63—64° (lit.,[1] 63—64°), δ (CDCl$_3$) 2.3 (6 H, s) and 7.02 and 7.55 (8 H, 2 × d, J 8 Hz), M$^+$ 312, m/e 221, 182, 167, and 91.

Decomposition of Tetrakis(pentadeuteriophenyl)tellurium.—Tetrakis(pentadeuteriophenyl)tellurium (0.045 g) was sealed in vacuo and heated in an oil-bath to its m.p. [102° (decomp., softening from 95°)]. The ampoule was cooled (−70 °C) and opened, and the contents, in ether (1.0 ml), were analysed by g.l.c. which indicated two equal components with retention times similar to those for biphenyl and diphenyl telluride. The mixture was separated by preparative g.l.c. (column C) into [^{2}H$_{10}$]biphenyl, m.p. 69—70° (from light petroleum), M$^+$ 164, m/e 82, and bis-(pentadeuteriophenyl)telluride as a yellow oil, M$^+$ 294, m/e 212, 164, 130, 128, and 82.

Decomposition of Tetraphenyl- and Tetrakis-(4-methylphenyl)-tellurium.—A mixture of tetraphenyl- and tetrakis-(4-methylphenyl)-tellurium (0.415 g), prepared by grinding to a powder tetraphenyltellurium (0.332 g) and tetrakis-(4-methylphenyl)tellurium (0.255 g), was sealed in vacuo (all operations performed under N$_2$) and plunged into an oil-bath at 140 °C. Decomposition occurred after a short induction period. The ampoule was cooled (−70 °C) and opened and the contents dissolved in ether (5 ml). G.l.c. indicated traces of benzene and toluene. Concentration afforded a reddish oil which was a mixture (g.l.c., n.m.r.) of six components which were separated by preparative g.l.c. (Table 4). Biphenyl, bitolyl, bis-(4-methylphenyl) telluride, and diphenyl telluride were identified by comparison on g.l.c. with authentic specimens, isolation and purification by preparative g.l.c., and comparison of n.m.r. and mass spectra with those of authentic specimens. p-Phenyltoluene was isolated by preparative g.l.c. as a low-melting solid which crystallised from ether–light petroleum (b.p. 30—40°) to m.p. 45—46° (lit.,[20] 49—50°), δ (CDCl$_3$) 2.36 (3 H, s), 7.18 and 7.48 (4 H, 2 × d, J 8—9 Hz), 7.2—7.7 (5 H, m), M$^+$ 168, m/e 153. Phenyl 4-methylphenyl telluride was isolated by preparative g.l.c. as an oil, δ (CDCl$_3$) 6.9—7.35 [5 H, d (δ 7.02), J 8 Hz, and m], 7.4—7.8 [4 H, d (δ 7.63), J 8 Hz, and m], and 2.31 (3 H, s), M$^+$

298; *m/e* 168. The telluride in cold benzene (3 ml) was treated with chlorine gas. The yellow solution was concentrated to a gum which crystallised on treatment with benzene–light petroleum (b.p. 40—60°)–ether as needles of phenyl-4-methylphenyltellurium dichloride, m.p. 130—131° (lit.,[1] 135—136°), *m/e* 298 and 168. Tetraphenyltellurium and tetrakis-(4-methylphenyl)tellurium in the ratio of 1.18 : 1 were allowed to react in dry toluene under nitrogen

TABLE 4

Products from decomposition of tetraphenyl- and tetrakis-(4-methylphenyl)-tellurium

Component	Retention time (s) (Column B)	Ratio (peak area) (no solvent)	(toluene/ N_2)
Biphenyl	72	3.5	1.64
p-phenyltoluene	111	3.5	2.58
Bitolyl	156	1	1
Diphenyl telluride	240	2.6	1.19
Phenyl 4-methylphenyl telluride	312	4.2	2.99
Bis-(4-methylphenyl) telluride	570	2.5	1.47

and afforded the same products, the ratio of which was determined by peak areas (Table 4).

Decomposition of Tetraphenyl- and Tetrakis(pentadeuteriophenyl)-tellurium.—A mixture (0.241 4 g) of tetrakis-(pentadeuteriophenyl)tellurium and tetraphenyltellurium (ratio 1 : 1.56) was sealed *in vacuo* and plunged into an oil-bath at 130 °C. When decomposition was complete, the ampoule was cooled and opened, and the contents, in ether (2 ml), were analysed by g.l.c. which indicated a two-component mixture with retention times similar to those for biphenyl and diphenyl telluride. The two components were isolated by preparative g.l.c. (column C) and analysed by mass spectrometry (Table 5).

Decomposition of Tetrakis-(4-methylphenyl)tellurium in

TABLE 5

Products for decomposition of tetraphenyl- and tetrakis(pentadeuteriophenyl)-tellurium

Component	M^+	*m/e*	Ratio (Peak height)
Biphenyls	164		1
	159		2.7
	154		2.6
Diphenyl tellurides	294	164	1
	289	159	2.5
	284	154	1.78

Diphenyl Telluride.—Tetrakis-(4-methylphenyl)tellurium (0.066 4 g) and diphenyl telluride (0.264 g) were sealed *in vacuo* and heated to 145 °C. The ampoule was cooled and opened, and the contents made up to 2 ml in benzene. The mixture (g.l.c.) contained six components which were identified by comparison of their retention times with those of authentic specimens (Table 6).

Bis-(4-methylphenyl) Telluride and Diphenyl Telluride.—Bis-(4-methylphenyl) telluride (4.3 mg) and diphenyl telluride (18.2 mg) were sealed *in vacuo* and heated to 140 °C (30 min). Comparison of g.l.c. traces of the mixture before and after heating indicated no formation of phenyl 4-methylphenyl telluride.

Control Reaction of Styrene with Dibenzoyl Peroxide.—Styrene (0.8 g) (distilled at 48° and 20 mmHg) was treated with dibenzoyl peroxide (51 mg) and heated to 120 °C under

N_2 (15 min). Removal of styrene *in vacuo* afforded polymeric material (0.654 g).

Comparative Study of Decomposition of Tetrakis-(4-methylphenyl)tellurium in the Presence of 1,4-Dihydrobenzene and in the Absence of Solvent.—Tetrakis-(4-methylphenyl)-tellurium (0.119 4 g) in a mixture of benzene and 1,4-dihydrobenzene [21] (2 : 1 v/v; 1.5 ml) was sealed under N_2 and heated to 140 °C together with a control experiment (0.032 3 g) under nitrogen. The ampoules were cooled and opened, and the contents made up to 2 and 1 ml, respectively, with benzene and analysed by g.l.c. Toluene was determined on column A by comparison of peak heights with those of standard solutions of toluene in benzene. The ratio of 4,4'-dimethylbiphenyl to bis-(4-methylphenyl)telluride was determined from average peak areas on column B (Table 2).

Decomposition of Phenylazotriphenylmethane (PAT) [22] *in Toluene.*—PAT (0.846 4 g) in dry toluene (5 ml) was sealed under nitrogen and heated at 100 °C for 1.45 h, when t.l.c. indicated total decomposition. The mixture was diluted to 10 ml with toluene and analysed for benzene (56%) by comparison of peak heights with those of standard solutions of benzene in toluene (column A). Removal of toluene gave a mixture (t.l.c.) of triphenylmethane (38%, determined by comparison of peak area with that of standard solutions in ether), diphenylmethane [19%, identified by comparison of retention time on g.l.c. with that of authentic material

TABLE 6

Products from decomposition of tetrakis-(4-methylphenyl)tellurium in diphenyl telluride

Component	Retention time (s) [a]	Ratio (peak area)
Biphenyl	91	1
p-Phenyltoluene	120	3.4
Bitolyl	156	12.1
Diphenyl telluride	233	*b*
Phenyl 4-methylphenyl telluride	346	22.7
Bis-(4-methylphenyl) telluride	578	7.8

[a] Column B.   [b] Solvent peak.

(column B, 240 °C) and estimated by comparison of the methylene singlet (δ 3.85) with that of triphenylmethane (δ 5.45) in the n.m.r. spectrum of the crude reaction mixture], *o*-phenyltoluene [8.5%; isolated by preparative g.l.c., identified by i.r. and mass spectra (M^+ 168) and estimated by comparison of peak area with that of standard solutions (column B)], and *p*-phenyltoluene [4.5%; isolated by preparative g.l.c.; identical (i.r., m.s., n.m.r.) to an authentic sample; estimated by comparison of peak area with that of standard solutions (column B)].

Decomposition of Tolylazotriphenylmethane (TAT) [22] *in the Presence of 1,4-Dihydrobenzene.*—TAT (0.274 7 g) in benzene–1,4-dihydrobenzene [21] (2 : 1 v/v, 2 ml) was sealed under nitrogen and heated at 80 °C for 2 h. The ampoule was cooled and opened and the contents made up to 5 ml with benzene. G.l.c. indicated formation of toluene (80%) and triphenylmethane (column B) (100%).

Decomposition of PAT in Furan.—PAT (0.21 g) in dry furan (2 ml) was sealed under nitrogen. The mixture was heated at 80 °C for 2 h when the solution became colourless. G.l.c. indicated the presence of benzene (4%) (column A) and triphenylmethane (35%) (column B). Removal of solvent afforded a glass (0.208 5 g) which was a mixture of triphenylmethane and a major component (lowest R_F) which was

isolated by preparative t.l.c. [silica gel; developed with light petroleum (b.p. 40—60°) and 1 : 1 v/v benzene–light petroleum (b.p. 40—60°)] as a gum (0.146 3 g) which was a mixture of isomeric 2-phenyl-5-triphenylmethyl-2,5-dihydrofurans m/e 386, 319, 320, 243, and 165. The gum, in benzene, was refluxed with dichlorodicyano-p-benzoquinone for 12 h to give a mixture which was chromatographed on a column (silica gel, eluted with light petroleum and 1 : 1 v/v benzene–light petroleum) to give 2-phenyl-5-triphenylmethylfuran, m.p. 109—111° (lit., 115—116°) δ 6.05 (1 H, d, 3.5 Hz), 7.54 (d, J 3.5 Hz), and 6.8—7.8 (m).

Reaction of Diphenyl Tellurium Dichloride with β-Phenylethylmagnesium Bromide.—Diphenyltellurium dichloride (1 g) in benzene (45 ml) was added rapidly to an ethereal solution of β-phenylethylmagnesium bromide [from β-phenylethyl bromide (2.62 g) and magnesium (0.5 g) in ether (15 ml)] at 5 °C under N_2. After 15 min the mixture was hydrolysed (10% hydrochloric acid). The organic layer was separated and the aqueous layer was washed with chloroform (2 × 10 ml). The washings were combined with the benzene, dried (Na_2SO_4), and concentrated to an oil which crystallised upon trituration with benzene–light petroleum (b.p. 40—60°) to give after filtration a crystalline solid A (0.988 g). Evaporation of the filtrate gave an oil B. The solid A (0.4 g) consisted of two components which were isolated by preparative t.l.c. (silica gel; 1 : 10 v/v ethanol–chloroform). The component with higher R_F was crystallised twice from benzene–light petroleum (b.p. 40—60°) to afford colourless plates of *tris*-(β-*phenylethyl*)*telluronium bromide* (0.273 g), m.p. 126—127°, δ (CDCl₃) 3.02 (12 H, s) and 7.2 (15 H, s), $v_{max.}$ (CHCl₃) 3 380, 2 900, 1 600, 1 490, 1 450, 1 400, 1 150, 1 125, and 920 cm⁻¹, m/e 340, 185, and 187 (Found: C, 55.0; H, 5.25. $C_{24}H_{27}BrTe$ requires C, 55.1; H, 5.15%). The lower-R_F component (0.083 g) crystallised from benzene–light petroleum (b.p. 40—60°) as colourless prisms of *tris*-(β-*phenylethyl*)*telluronium chloride*, m.p. 134—135°, δ (CDCl₃) 3.02 (12 H, s) and 7.2 (15 H, s,) $v_{max.}$ (CHCl₃) 3 320, 2 900, 1 600, 1 490, 1 450, 1 400, 1 150, 1 130, and 920 cm⁻¹; m/e 340, 140, and 142 (Found: C, 60.35; H, 5.7; Cl, 7.4. $C_{24}H_{27}ClTe$ requires C, 60.25; H, 5.65; Cl, 7.4%). Oil B was a mixture (t.l.c.) of the telluronium salts with 1,4-diphenylbutane and diphenyl telluride which ran as a single upper component in light petroleum. The upper components after separation by preparative t.l.c. [silica gel; light petroleum (b.p. 40—60°)] were isolated as an oil (0.27 g) which upon treatment with sulphuryl chloride in carbon tetrachloride afforded prisms of diphenyltellurium dichloride (0.106 g), identical (n.m.r., t.l.c., m.p.) to an authentic specimen. The filtrate afforded an oil which crystallised from light petroleum (b.p. 40—60°) upon cooling as prisms of 1,4-diphenylbutane (0.08 g), identical to an authentic specimen (n.m.r., t.l.c., m.p.).

Tris-(β-*phenylethyl*)*telluronium Bromide.*—The preceding reaction was repeated on a half-molar scale. The mixture was stirred overnight at room temperature and then at 35 °C for 2 h, when t.l.c. indicated no telluronium salts to be present. Work-up produced an oil (0.782 g) which was a mixture (t.l.c.). The oil was diluted to 5 ml with benzene and analysed for 1,4-diphenylbutane (30%) on g.l.c. (column B) by comparison of peak area with that of standard solutions of 1,4-diphenylbutane in benzene.

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